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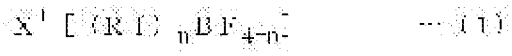
(54) ELECTROLYTIC SOLUTION AND ELECTROCHEMICAL ELEMENT USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolytic solution with P less tendency to generate hydrogen fluoride by hydrolysis.

SOLUTION: Boron compound(s) shown in a formula 1 (X+[(Rf) nBF4-n]- is dissolved in a non-aqueous solvent. In the formula, X+ shows alkali metal ion or onium ion, Rf shows perfluoroalkyl group, and n shows integer of 1 to 4. When n is not less than 2, plural Rfs may be mutually different and plural Rfs may be mutually bonded to form a ring structure together with boron.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to electrochemical elements, such as an electrolysis solution which the boron compound containing fluoride is dissolving in the nonaqueous solvent and a lithium cell using this electrolysis solution, an electric double layer capacitor, and an aluminium electrolytic capacitor.
[0002]
[Description of the Prior Art]As nonaqueous electrolyte used for an electrochemical element, many things are known from the former. for example, the thing (Masayuki Yoshio.) which dissolved lithium hexafluorophosphorate in the mixed solvent of ethylene carbonate and diethyl carbonate as nonaqueous electrolyte of a lithium cell What dissolved Nikkan Kogyo Shimbun and perfluoroalkyl lithium fluorophosphorate in ethyleneglycol dimethyl ether etc. (WO 98/No. 15562 gazette) is known in the volume for Akiya Ozawa, a rechargeable lithium-ion battery, Chapter 6, 83 pages, and 1996. As an electrolysis solution of an electric double layer capacitor, what dissolved quarternary ammonium salt of tetrafluoroboric acid in propylene carbonate etc. (Makoto Ue, electrochemistry, 66 **, 904 pages, 1998) is known. As an electrolysis solution of an aluminium electrolytic capacitor, quarternary ammonium salt (Makoto Ue et al. and a new capacitor.) of organic acid, such as phthalic acid What dissolved 3 **, No. 2, 55 pages, 1996, and the fourth class friend JINIUMU salt in gamma-butyrolactone, ethylene glycol, etc. (WO 95/No. 15572 gazette, JP,9-283379,A) is known.
[0003]
[Problem(s) to be Solved by the Invention]The nonaqueous electrolyte used for an electrochemical element is manufactured so that the moisture content may decrease as much as possible, but it usually still contains the moisture of tens of ppm. Since the moisture which the moisture in atmosphere might mix into nonaqueous electrolyte, and has adhered to the parts of an electrochemical element, etc. may be eluted in nonaqueous electrolyte when manufacturing an electrochemical element using nonaqueous electrolyte, The moisture of not less than tens of ppm exists, so that it may certainly say the nonaqueous electrolyte used for the electrochemical element.

[0004]When moisture exists in the nonaqueous electrolyte used for the electrochemical element, there is a problem that the electrolyte which is dissolving is hydrolyzed. For example, it hydrolyzes like a lower type and the lithium hexafluorophosphorate used for the nonaqueous electrolyte of the lithium secondary battery generates hydrogen fluoride.

$LiPF_6+H_2O \rightarrow LiF+POF_3+2HF$ hydrogen fluoride is rich in reactivity, and causes the reaction of making the metal part of an electrochemical element corrode, or making nonaqueous electrolyte disassemble etc. which is not preferred. If these reactions occur, the various characteristics of an electrochemical element, for example, electric capacity, charge and discharge efficiency, withstand voltage, etc. will fall, or appearance defects, such as expansion of the element by the generation of gas, will happen. Therefore, even if a small amount of moisture exists, the nonaqueous electrolyte which cannot cause hydrolysis easily is called for. This invention tends to meet such a demand.

[0005]

[Means for Solving the Problem]A boron compound shown by a formula (1) in a nonaqueous solvent is dissolving an electrolysis solution concerning this invention.

$X^+[(Rf)_nBF_{4-n}]^-$ -- (1)

X^+ shows alkali metal ion or onium ion among [type, Rf shows a perfluoroalkyl group, and n shows an integer of 1 thru/or 4. When n is two or more, it may differ mutually, and two or more Rf may join mutually together, and two or more Rf may form a ring structure with boron.]

[0006]

[Embodiment of the Invention]In the electrolysis solution concerning this invention, the boron compound containing the fluoride shown by the above-mentioned formula (1) is used as an electrolyte. As a cation shown by X^+, for example Lithium, sodium, Alkali metal cations, such as potassium and caesium; Tetramethylammonium, Ethyl trimethylammonium, diethyl dimethylannmonium, triethyl methylammonium, Tetraethylammonium, tetrapropylammonium, tetrabutylammonium, N,N-dimethylpyrrolidinium, N-ethyl-N-methyl pyrrolidinium, Fourth class ammonium cation;1-ethyl-2-methyl imidazolium, such as N,N-dimethyl piperidinium and N-ethyl-N-methyl piperidinium, The fourth class friend JINIUMU cations, such as 1-ethyl-2,3-dimethyl imidazolinium, 1, 2 and 3, and 4-tetramethyl imidazolinium; Tetramethylphosphonium, The fourth class phosphonium cations, such as ethyl trimethyl phosphonium, diethyldimethyl phosphonium, triethylmethyl phosphonium, tetraethyl phosphonium, tetrapropyl phosphonium, and tetrabutylphosphonium, etc. are mentioned. As for X^+, in the case of the electrolysis solution of a lithium cell, it is especially preferred that it is a lithium ion. In the case of the electrolysis solution of an electric double layer capacitor, it is preferred that they are the fourth class friend JINIUMU ion, such as 1-ethyl-2,3-dimethyl imidazolinium, in the case of the electrolysis solution of the fourth class ammonium ion, such as triethyl methylammonium, and an aluminium electrolytic capacitor.

[0007]As a perfluoroalkyl group shown by Rf, A trifluoromethyl group, a pentafluoroethyl group, a heptafluoro propyl group, Perfluoroalkyl groups of the carbon numbers 1-12, such as a

nonafluorobutyl group, an undecafluoropentyl group, a perfluoro hexyl group, a perfluoro octyl group, a perfluoro decyl group, and a perfluoro undecyl group, are mentioned. As what two or more Rf combined mutually, an octafluoro tetramethylen group, a decafluoro pentamethylene group, etc. are mentioned. (1) As for the sum total of carbon of the fluorinated hydrocarbon group shown by Rf, in the compound of a formula, it is preferred that it is 12 or less. As an example of (1)-type compound which has these fluorinated hydrocarbon groups, Trifluoromethyl trifluoro borate, bis(trifluoromethyl)difluoro borate, Tris (trifluoromethyl) fluoroborate, tetrakis (trifluoromethyl) borate, Pentafluoroethyl trifluoro borate, bis(pentafluoroethyl)difluoro borate, Tris (pentafluoroethyl) fluoroborate, tetrakis (pentafluoroethyl) borate, Heptafluoro propyltrifluoro borate, bis(heptafluoro propyl)difluoro borate, Tris (heptafluoro propyl) fluoroborate, tetrakis (heptafluoro propyl) borate, Nonafluoro butyltrifluoro borate, bis(nonafluoro butyl)difluoro borate, Tris (nonafluoro butyl) fluoroborate, undecafluoro PENCHIRUTORI fluoroborate, Bis(undecafluoropentyl)difluoro borate, perfluoro hexyltrifluoro borate, bis(perfluoro hexyl)difluoro borate, perfluoro octyltrifluoro borate, Perfluoro decyltrifluoro borate, perfluoro undecyltrifluoro borate, Trifluoromethyl pentafluoroethyl difluoro borate, bis(trifluoromethyl) pentafluoroethyl fluoroborate, Tris (trifluoromethyl) pentafluoroethyl borate, trifluoromethyl bis (pentafluoroethyl)fluoroborate, Bis(trifluoromethyl)bis(pentafluoroethyl)borate, Trifluoromethyl tris (pentafluoroethyl) fluoroborate, Tetrakis (pentafluoroethyl) borate, perfluoro (B,B-tetramethylen) difluoro borate, Perfluoro [bis(B,B-tetramethylen)borate], perfluoro (B,B-pentamethylene) difluoro borate, perfluoro [bis(B and B-pentamethylene)borate], etc. are mentioned. Generally, (1)-type compound is in the tendency for the electrical conductivity of the electrolysis solution which makes this an electrolyte to fall as a molecular weight becomes large. Therefore, as an electrolyte, it is preferred to use trifluoromethyl trifluoro borate or bis(trifluoromethyl)difluoro borate. (One)-type compound can also use two or more sorts together.

[0008](1) The compound shown by a formula is compoundable by a publicly known method. For example, trifluoromethyl trifluoro borate is compoundable to R.D.Chambers et al., J.Am.Chem.Soc., and 82 and 5298 (1960) by the method of a statement. Bis(trifluoromethyl)difluoro borate is compoundable to G.Pawellke et al., J.Organomet.Chem., and 178 and 1 (1979) by the method of a statement. The cation (X^+) of the compound shown by (1) formula is convertible for other cations by a publicly known proper method. For example, by distilling off a solvent, after considering it as the solution from which the solution of (1)-type compound was processed with H type cation exchange resin, and the cation was changed into the hydrogen ion and adding hydroxide of a desired cation, or the solution of a hydrogencarbonate to this, (One)-type compound which has a desired cation can be obtained. As an exception method, the salt of a desired cation is added in the solution of (1)-type compound, and after settling the cation of (1)-type compound as insoluble salt and removing it, (1)-type compound which has a desired cation can also be obtained by distilling off a solvent. (1) Since to be a high grade very much is demanded when using the compound of a formula as an electrolyte of an electrochemical element, refine and use even for desired purity (1)-type compound usually obtained by the above by recrystallization, solvent extraction, etc.

[0009]As a solvent of an electrolysis solution, for example Dimethyl carbonate, ethyl carbonate

methyl, diethyl carbonate, Diphenyl carbonate, carbonic acid methylphenyl, ethylene carbonate, propylene carbonate, Carbonic ester, such as 2,3-dimethylethylene carbonate, butylene carbonate, vinylene carbonate, and 2-vinylethylene carbonate; Methyl formate, Methyl acetate, methyl propionate, ethyl acetate, propyl acetate, butyl acetate, Amyl acetate, methyl benzoate, ethyl benzoate, gamma-butyrolactone, Carboxylate, such as gamma-valerolactone and delta-valerolactone; Ethyleneglycol dimethyl ether, Ethylene glycol diethylether, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, 1,4-dioxane, 1,3-dioxolane, A tetrahydrofuran, 2-methyltetrahydrofuran, a 2,6-dimethyltetrahydrofuran, Ether, such as tetrahydropyran, ethylene glycol, propylene glycol, Alcohols, such as glycerin; Nitril;N-methylformamides, such as acetonitrile, propionitrile, methoxy propionitrile, glutaronitrile, an adiponitrile, and 2-methylglutaronitrile. N-ethylformamide, N.N-dimethylformamide, N,N-dimethylacetamide, Amide, such as N-methylpyrrolidinone; A dimethylsulfone, an ethylmethylsulfone, Sulfones, such as diethyl sulfone, sulfolane, 3-methyl sulfolane, and 2,4-dimethylsulfolane; Dimethyl sulfoxide, Sulfoxides, such as a methylethyl sulfoxide and diethyl sulfoxide; Dimethyl sulfate, Sulfate ester, such as diethyl sulfate, sulfuric acid ethylene, and sulfuric acid propylene; Sulfurous acid dimethyl, Sulfites, such as sulfurous acid diethyl, sulfurous acid ethylene, and sulfurous acid propylene; Trimethyl phosphate, Phosphoric ester, such as phosphoric acid ethyldimethyl, diester phosphate methyl, and phosphoric acid triethyl; 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl- 3,4,5,6-tetrahydro 2(1H)-pyrimidinone, 3-methyl-2-oxazolidinone, nitromethane, etc. are mentioned. These solvents can also use two or more sorts together. It is preferred that make carbonic ester, carboxylate, or these into a subject also in these solvents, namely, 50 % of the weight or more uses what is carbonic ester and carboxylate.

[0010]The electrolysis solution concerning this invention dissolves the boron compound containing the above-mentioned fluoride in the above-mentioned solvent. Since the higher one of the electrical conductivity of an electrolysis solution is generally preferred, the concentration of the boron compound in an electrolysis solution is a range which does not deposit by a temperature change etc., and its higher possible one is preferred. When using trifluoromethyl trifluoro borate and bis (trifluoromethyl)difluoro borate as a boron compound, the concentration of these compounds in an electrolysis solution is usually 0.1-3mol/L, and is 0.5-2mol/L preferably.

[0011]The electrochemical element concerning this invention carries out the placed opposite of an anode and the negative electrode via a separator fundamentally, and has the structure where it impregnated with the electrolysis solution prepared above by this. In the case of lithium ion batteries, such as a lithium primary battery, a rechargeable lithium-ion battery, and a lithium polymer secondary battery, As positive active material, $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, Multiple oxide;MnO_2 of lithium, such as $LiMn_2O_4$, and a transition metal, Transition metal sulfide, such as transition metal oxide;MoS_2, such as V_2O_5, and TiS; Polyacethylene, Conductive polymers, such as poly acene, poly aniline, polypyrrole, and a polythiophene; disulfide compounds, such as poly (2,5-dimercapto-1,3,4-thiadiazole), etc. are used. As negative electrode active material, a lithium metal and lithium alloys, such as a lithium aluminum alloy, Or corks, such as carbide of high molecular compounds, such as occlusion and the

carbonaceous material which can be emitted, for example, black lead, phenol resin, and furan resin, pitch coke, petroleum coke, and needle coke, carbon fiber, glassy carbon, pyrolytic carbon, activated carbon, etc. are used in lithium. It is preferred that a cation (X^+) uses what dissolved (1)-type compound which is lithium in the mixed solvent of cyclic carbonate, such as ethylene carbonate and propylene carbonate, and chain carbonic ester, such as dimethyl carbonate, ethyl carbonate methyl, and diethyl carbonate, as an electrolysis solution.

[0012]It is preferred to use a carbonaceous material as a material of the polarizable electrode used for an anode and a negative electrode in that are inertness electrochemically and it has moderate conductivity to an electrolysis solution in the case of an electric double layer capacitor. Activated carbon with a large area of the electrode interface which an electric charge accumulates is especially preferred. It is preferred that a cation (X^+) uses what dissolved (1)-type compound which is quaternary ammonium, the fourth class friend JINIUMU, or the fourth class phosphonium in propylene carbonate as an electrolysis solution.

[0013]In the case of an aluminium electrolytic capacitor, aluminium foil is used as the aluminium foil and the negative electrode which formed the insulating alumina layer in the surface by anodizing etc. as an anode. For expansion of surface area, the etching process of such aluminium foil is usually carried out, and it is used. It is preferred to use that by which the cation (X^+) dissolved (1)-type compound which is quaternary ammonium, the fourth class friend JINIUMU, or the fourth class phosphonium in gamma-butyrolactone, ethylene glycol, sulfolane, or ones of these mixed solvents as an electrolysis solution.

[0014]As a separator used for an electrochemical element, the product made of paper, the product made from polypropylene, the product made from polyethylene, the product made from glass fiber, etc. should just use a thing in ordinary use. As an electric conduction auxiliary agent used when manufacturing an electrode with an electrode active material, it is preferred to use metal fibers, such as carbon black, such as acetylene black and Ketchen black, natural graphite, thermal expansion graphite, carbon fiber, ruthenium oxide, titanium oxide, aluminum, and nickel, etc. It is especially desirable to use acetylene black or Ketchen black which can secure desired conductivity by a little combination. An electric conduction auxiliary agent is blended so that it may usually become 5 to 50 % of the weight to an electrode active material, but it is preferred to blend so that it may become 10 to 30 % of the weight.

[0015]As a binder used with an electric conduction auxiliary agent, It is preferred to use polytetrafluoroethylene, polyvinylidene fluoride, carboxymethyl cellulose, fluoro olefine copolymer crosslinked polymer, polyvinyl alcohol, polyacrylic acid, polyimide, a petroleum pitch, a coal pitch, phenol resin, etc. It is preferred to use the polymer (**) of polytetrafluoroethylene, polyvinylidene fluoride, and other fluoride content monomers or the copolymer of these monomers and other monomers especially. Since the dissolved electrolytes are water and difficulty reactivity, the electrolysis solution concerning this invention has the small tendency to generate hydrogen fluoride, even if a little water exists in an electrolysis solution. Therefore, the electrochemical element

manufactured using this electrolysis solution continues at a long period of time, is stabilized and can maintain that characteristic.

[0016]

[Example]Although an example explains this invention still more concretely below, this invention is not limited to these examples.

[0017]Electrolysis solution; the electrolysis solution was prepared using the solvent and electrolyte which are shown in Table 1, and the electric conductivity and the moisture content at 25 ** were measured. The content of hydrogen fluoride was measured by the ion chromatography method, the content of hydrogen fluoride was again measured about what held this electrolysis solution at 70 ** in the well-closed container made from stainless steel further for 50 hours, and the increase of stock of the hydrogen fluoride concentration by heating was computed. A result is shown in Table 1.

[0018]

[Table 1]

表 1

No.	電解液			電導度 (mS/cm)	水分量 (ppm)	HF量(ppm)		HF増加 (ppm)
	電解質	濃度 (mol/L)	溶媒			加熱前	加熱後	
1	$Li^+CF_3BF_3^-$	1.0	EC+DEC	8.8	18	10	15	5
2	$TEMA^+CF_3BF_3^-$	1.0	PC	7.1	30	65	67	2
3	$EDMI^+(CF_3)_2BF_2^-$	0.5	GBL	9.6	55	12	12	0
4	$Li^+PF_6^-$	1.0	EC+DEC	8.3	15	7	70	63
5	$TEMA^+BF_4^-$	1.0	PC	8.5	30	70	95	25

TEMA$^+$：トリエチルメチルアンモニウムカチオン

EDMI$^+$：1－エチル－2，3－ジメチルイミダゾリニウムカチオン

EC＋DEC：炭酸エチレンと炭酸ジエチルとの1:1(重量比)混合物

PC：炭酸プロピレン

GBL：γ－ブチロラクトン

[0019]Lithium secondary battery; lithium manganese multiple oxide ($LiMn_2O_4$) 90 weight section, acetylene black 5 weight section, and polyvinylidene fluoride 5 weight section were mixed, N-methylpyrrolidinone was added to this, and it was considered as the slurry. After applying and drying this at aluminium foil, it pierced in a circle 12.5 mm in diameter, and was considered as the anode. A separator (0.3-mm-thick porous polypropylene sheet) is passed to the case made from stainless steel (20 mm in diameter, and 1.6 mm in thickness), and they are an anode and a negative electrode (12.5 mm in diameter.). After accommodating the 1.0-mm-thick lithium metal board and carrying out vacuum impregnation of the electrolysis solution of NO.1 of Table 1 to this, the lid was put via the gasket made from polypropylene, and the ******** coin type lithium secondary battery was manufactured. When the charge and discharge test was done about this cell in charge and discharge current density 0.6mA/cm^2 and the voltage ranges 4.3-3.5V, initial service capacity was 123 mAh/g

and the charge and discharge efficiency of 20 cycle eye was 97%. On the other hand, when the examination same about the lithium secondary battery completely manufactured in a similar manner except having used the thing of NO.4 of Table 1 as an electrolysis solution was done, initial service capacity was almost the same at 122 mAh/g, but. The charge and discharge efficiency of 20 cycle eye was as low as 88%, and was large. [of cycle degradation]

[0020]Electric double layer capacitor; coconut-shell-activated-charcoal powder (specific surface area 1700m^2/g, mean particle diameter of 10 micrometers) 80 weight section, acetylene black 10 weight section, and polytetrafluoroethylene 10 weight section were mixed, it kneaded and molded, and the anode and the negative electrode were manufactured. An anode and a negative electrode are accommodated in the case made from stainless steel (20 mm in diameter, and 1.6 mm in thickness) via a separator (0.3-mm-thick nonwoven fabric made from polypropylene), After carrying out vacuum impregnation of the electrolysis solution of NO.2 of Table 1 to this, the lid was put via the gasket made from polypropylene, and the ******** coin type electric double layer capacitor was manufactured. The constant-voltage continuation impression examination was done over 50 hours with 70 ** and the impressed electromotive force 3.0V about this, and change of electric capacity was investigated. The electric capacity computed from the constant-current-discharge curve in 5 mA is 1.3F before an examination.

The electric capacity maintenance factor after an examination was 98%.

On the other hand, when the examination same about the electric double layer capacitor completely manufactured in a similar manner except having used the thing of NO.5 of Table 1 as an electrolysis solution was done, the electric capacity before an examination was the same as 1.3F, but the electric capacity maintenance factor after an examination was as low as 92%, and its degradation was comparatively large.

[0021]The capacitor made from aluminum; Case size [of 10 mm] phix16mmL, The aluminum electrolytic capacitor element of the rated voltage 10V and rated electric capacity 1000F specification (with the etched aluminium foil which has on the surface an alumina layer which is a dielectric.) Vacuum impregnation of the electrolysis solution of NO.3 of Table 1 was carried out to what stopped the separator made of paper, and the etched aluminium foil on winding and a tape. This was accommodated in the case made from aluminum via the obturation rubber made of isobutylene isoprene rubber, and the CEO4 type aluminium electrolytic capacitor was manufactured by caulking ******. When the load test of 1000 hours was done at 105 ** about this thing and the impedance at 100 kHz was measured, examination before was 0.05 ohm and the examination back was 0.07ohm. on the other hand, the thing (the electric conductivity at 25 ** -- 9.1 mS/cm) which is used from the former as an electrolysis solution and which dissolved 1-ethyl-2,3-dimethyl imidazolinium phthalic acid hydrogen salt in gamma-butyrolactone so that it might be set to 0.5 mol / L When the aluminium electrolytic capacitor completely manufactured in a similar manner except having used the moisture content of 50 ppm did the same examination, the impedance before an examination was 0.05ohm, but the impedance after an examination was increasing to 0.10 ohm.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1]An electrolysis solution, wherein a boron compound shown by a formula (1) in a nonaqueous solvent is dissolving.

$X^+[(Rf)_nBF_{4-n}]^-$ -- (1)

X^+ shows alkali metal ion or onium ion among [type, Rf shows a perfluoroalkyl group, and n shows an integer of 1 thru/or 4. When n is two or more, it may differ mutually, and two or more Rf may join mutually together, and two or more Rf may form a ring structure with boron.]
[Claim 2]An electrolysis solution, wherein a boron compound shown by a formula (2) in a nonaqueous solvent is dissolving.

$X^+[(CF_3)_mBF_{4-m}]^-$ -- (2)

X^+ shows alkali metal ion or onium ion among [type, and m shows 1 or 2.]

[Claim 3]The electrolysis solution according to claim 1 or 2, wherein X^+ is the ion chosen from a group which comprises a lithium ion, the fourth class ammonium ion, and the fourth class friend JINIUMU ion.
[Claim 4]The electrolysis solution according to any one of claims 1 to 3, wherein ester as which a nonaqueous solvent was chosen from a group which comprises carbonic ester and carboxylate is what occupies 50 % of the weight or more.
[Claim 5]An electrochemical element using the electrolysis solution according to any one of claims 1 to 4.
[Claim 6]The electrochemical element according to claim 5, wherein an electrochemical element is a lithium secondary battery, an electric double layer capacitor, or an electrolytic condenser.

[Translation done.]